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(54) Title: SHAPE MEMORY POLYMERS BASED ON SEMICRYSTALLINE THERMOPLASTIC POLYURETHANES BEAR-
ING NANOSTRUCTURED HARD SEGMENTS

(57) Abstract: Thermoplastic polyurethanes having an alternating sequence of hard and soft segments in which a nanostructured
polyhedral oligomeric silsesquioxane diol is used as a chain extender to form a crystalline hard segment constituting SMPs. The
polyurethanes are formed by reacting a polyol, a chain extender dihydroxyl-terminated POSS and a diisocyanate. The polyurethanes
have multiple applications including for example, important for human health care, drug delivery matrices, superabsorbant hydrogels,
coatings, adhesives, temperature and moisture sensors, etc.

SHAPE MEMORY POLYMERS BASED ON SEMICRYSTALLINE THERMOPLASTIC POLYURETHANES BEARING NANOSTRUCTURED HARD SEGMENTS

Cross-Reference To Related Applications

This application claims the priority of Provisional Applications Serial Nos. 60/418,023 filed October 11, 2002, 60/466,401 filed April 29, 2003; Serial No. 60/419,506 filed October 18, 2002; 60/488,590 filed July 18, 2003 and 60/488,323 filed July 18, 2003, each of which is are incorporated herein in their entirety by reference thereto. Both application Serial No. 10/425,421 filed April 29, 2003 which claims priority from provisional application Serial No. 60/377,544 and the claimed provisional applications are also incorporated herein by reference.

Technical Field

The instant disclosure relates to shape memory polymers and more particularly thermoplastic polyurethanes with an alternating sequence of hard and soft segments in which a nanostructured polyhedral oligomeric silsesquioxane diol is used as a chain extender to form a crystalline hard segment and also relates to methods for the preparation of these thermoplastic polyurethanes and to applications thereof..

Background of the Disclosure

Shape memory materials feature an ability to transform shape from a temporary, frozen, shape to a permanent shape when triggered by an environmental stimulus, such as heat, light, or vapor. Used creatively, these phenomena can be exploited for a wide range of applications. While both shape memory alloys (SMAs) and shape memory polymers (SMPs) show similar thermo-stimulated shape memory properties, their mechanisms of action are quite distinct. Advantages of SMAs include rapid strain recovery (within 1 second), the potential training for two-way reversible memory, and an apparent superelasticity due within the austentite phase at low temperature. In contrast, polymers intrinsically exhibit shape memory effects derived from their highly coiled constituent chains that are collectively extensible via mechanical work and this energy may be stored

indefinitely, known as "shape fixing," by cooling below T_g or T_m. The polymeric samples
can later perform mechanical work and return to a stress-free state when heated above the
critical temperature, mobilizing the frozen chains to regain the entropy of their coiled
state. In comparison to SMAs, thermally stimulated SMPs have the advantages of: (i)
large recoverable deformations in excess of several hundred percent strain; (ii) facile
tuning of transition temperatures through variation of the polymer chemistry; and (iii)
processing ease at low cost.

Thermally stimulated SMPs with different thermomechanical properties to
function in various applications, for example as medical devices and mechanical
actuators have previously been synthesized and characterized. The materials span a
range of room temperature moduli, from rigid glassy materials having storage moduli of
several GPa to compliant rubbers with moduli as low as tens of MPa. Moreover, the
retracting (rubbery) moduli have been adjusted over the range $0.5 < E < 10$ MPa, as
prescribed by the end application. One such example is chemically crosslinked
polycyclooctene (PCO), a stiff semicrystalline rubber that is elastically deformed above
T_m to a temporary shape that is fixed by crystallization. Fast and complete recovery of
gross deformations is achieved by immersion in hot water. These SMPs have been
described in Provisional Patent Application Serial No. 60/419,506 filed October 18, 2002
entitled Chemically Crosslinked Polycyclooctene, the entirety of which is incorporated
herein by reference. In Provisional Patent Application Serial No. 60/377,544 filed May
2, 2002 entitled Castable Shape Memory Polymers, the entirety of which is incorporated
herein by reference, stiffer SMPs offering tunable critical temperatures and rubber
modulus using a thermosetting random copolymer made of two vinyl monomers that
yield controlled T_g and casting-type processing are described. Such copolymers were
crosslinked with a difunctional vinyl monomer (crosslinker), the concentration of
crosslinker controlling the rubber modulus and thus the work potential during recovery.
Besides their shape memory effects, these materials are also castable allowing for
processing more complex shapes. In addition, they are optically transparent making them
useful for additional applications.

The use of chemical crosslinking in both of these cases limits the types of processing possible and forever sets the equilibrium shape at the point of network formation. Therefore, miscible blends of a semicrystalline polymer with amorphous polymers have also been intensively investigated due to their attractive crystalline properties and mechanical properties. For those blends that are miscible at the molecular level, a single glass transition results, without broadening, an aspect important to shape memory. Additionally, in such miscible blends the equilibrium crystallinity (which controls the plateau modulus between T_g and T_m where shape fixing is performed) also changes dramatically and systematically with the blend compositions. It provides a simple route to alternative shape memory plastics; i.e. SMPs with relatively high modulus in the fixed state at room temperature, having a tunable and sharp transition, and the permanent shape can be remolded repeatedly above certain melting temperatures. These SMP blends have been described in Provisional Patent Application Serial No 60/466,401 filed April 29, 2003 entitled Blends of Amorphous and Semicrystalline Polymers with Shape Memory Properties, the entirety of which is incorporated herein by reference.

Microphase-separated semicrystalline thermoplastic polymers with two sharp melting transitions $T_{m2} > T_{m1} >$ room temperature, where the difference of the two melting points is at least 20 °C, are also good candidates for shape memory offering the advantage of melt processing above T_{m2}, and repeated resetting of the equilibrium shape by relaxing stress in the fluid state. Representative past examples of such polymers in this class of SMP are conventional polyurethanes whose soft domains are glassy or semicrystalline with low melting point (but higher than T_{crit}) and whose hard domains feature a higher melting point only exceeded during processing.

Objects of the Disclosure

It is an object of the present disclosure to provide shape memory polymers comprising hybrid polyurethanes.

It is another object of the disclosure to provide shape memory polymers having medium and tunable modulus in the fixed state at room temperature, having a tunable and

sharp transition, whose permanent shape can be repeatedly remolded above a certain melting temperature.

It is another object of the disclosure to provide hybrid polyurethane SMPs evidencing sharp and tunable transition temperatures, adjustable stiffness above their transition temperatures and thermal processability above the melting point of the POSS domains.

It is yet another object of the disclosure to provide hybrid polyurethane SMPs which possess excellent shape recovery effect at the recovery temperature and wherein the retracting force is adjustable according to the composition of the POSS.

Still a further object of the disclosure is to provide hybrid polyurethanes that are biocompatible and can be used as medical devices and implants.

Yet another object of the disclosure is a method for synthesizing such hybrid polyurethanes.

Summary

Broadly the disclosure provides a method for producing hybrid polyurethane SMPs by reacting (A) a polyol, (B) a chain extender dihydroxyl-terminated POSS and (C) a diisocyanate., wherein POSS stands for a polyhedral silsesquioxane diol. The polyol (A) can be polyethylene glycol (PEG), polycaprolactone (PCL), polycyclooctene (PCO), trans-1,4 butadiene, transisoprene, polynorbornene diol and polymethacrylate copolymer, the chain extender(B) can be TMP cyclopentyldiol-POSS, TMP cyclohexyldiol-POSS, TMP isobutyldiol-POSS, trans-cyclohexanediolcyclohexane-POSS, or transcyclohexanediolisobutyl-POSS. and the diisocyanate (C) can be selected from a large number of diisocyanates and is preferably 4,4' diphenyl methylene diisocyanate (MDI). Other diisocyanates (C) that are suitable for use in the synthesis of hybrid polyurethane SMPs include: toluene-2,4-diisocyanate (TDI), toluene-2,6diisocyanate, hexamethylene-1,6-diisocyanate (HDI), 4,4'diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI), and hydrogenate 4,4'-diphenylmethane diisocyanate (H12MDI).

The polyol can be semicrystalline and preferably selected from polyethylene glycol (PEG), polycaprolactone (PCL), polycyclooctene (PCO), trans-1,4 butadiene, transisoprene or it can be amorphous in which case it can be polynorbornene diol and/or polymethacrylate copolymer.

The method for producing hybrid polyurethane SMPs and the novel hybrid polyurethanes prepared thereby are illustrated by the following non-limiting reaction schemes.

Scheme 1.
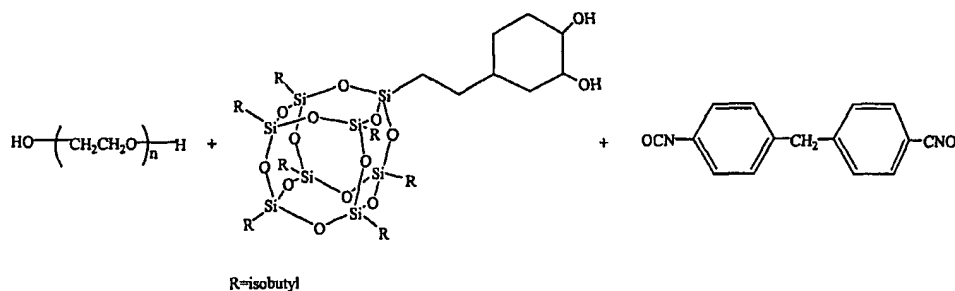
R=isobutyl

This scheme shows an example of synthesis of TPU using polyethylene glycol as polyol, TMP Isobutyldiol-POSS as chain extender to react with 4,4' diphenyl methylene diisocyanate in toluene.

Scheme 2.
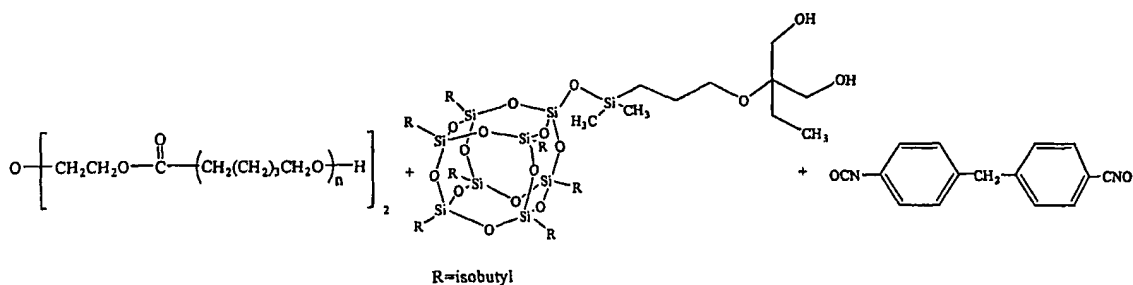
R=isobutyl

This scheme shows an example of synthesis of TPU using polycaprolactone diol as polyol, TMP Isobutyldiol-POSS as chain extender to react with 4,4' diphenyl methylene diisocyanate.

Scheme 3.

R=isobutyl

This scheme shows an example of synthesis of TPU using polyocyclooctene as polyol, TMP Isobutyldiol-POSS as chain extender to react with 4,4' diphenyl methylene diisocyanate.

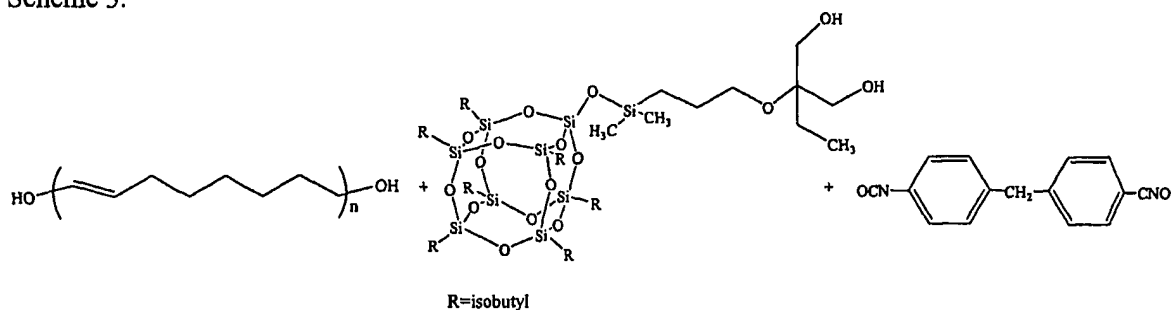A general formula for the POSS-based TPUs incorporating PEG diol, prepared according to Scheme 1, follows. The polymers allow systematic variation in the ratio of X/Y (1 to 20), the polyol degree of polymerization ($1 < n < 1000$), and the total degree of polymerization, $2 < m < 100$.
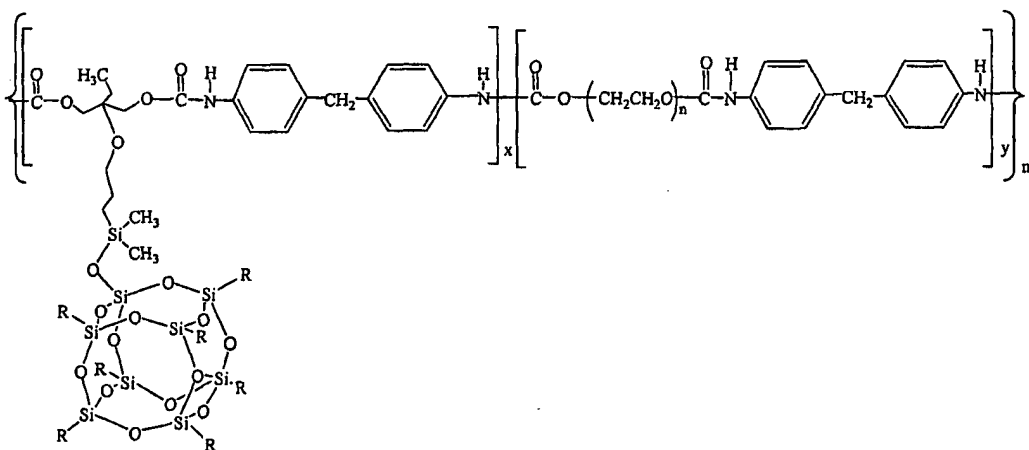
The instant hybrid polyurethanes demonstrate sharp and tunable transition temperatures, adjustable stiffness above their transition temperatures, and thermal

processibilty above the melting point of the POSS domains. The hybrid polyurethanes
also show excellent shape recovery effect at the recovery temperature and a retracting
force which is adjustable according to the composition of the POSS. They also posses a
unique property that is different from the other shape memory polymers in that the
current disclosure (in the PEG embodiment) can be triggered to recover by moisture
(liquid or vapor) in addition to heating. For the thermal triggering mechanism, the range
30 °C to 60 °C according to the ratio of the components used and (importantly) thermal
annealing to achieve steady-state (equilibrium) crystallinity is important . The recovery
can be finished within seconds when heated 20 °C above the transition temperature. The
additional advantages of the materials include that the materials are rigid at room
temperature, the polymers generally are biocompatible and in some cases biodegradable
and can be used as medical devices and implants. The products also can be dyed to any
color or rendered radio-opaque for d-ray radiography according to application
requirements.

Any of the hybrid polyurethane polymers mentioned above may be filled with, for
example, nanoparticles of boron nitride, silica, titanium dioxide, montmullinite, clay,
Kevlar, staple, aluminum nitride, barium and bismuth subcarbonate. Clay and silica can
be used to, for example, increase the modulus of the plastic. Dispersing agents and/or
compatibilizing agents may be used, for example, to improve the blending of polymers
and the blending of polymers with fillers. Dispersing agents and/or compatibilizing
agents include, for example, ACRAWAX® (ethylene bis-stearamide), polyurethanes and
ELVALOY® (acrylic functionalized polyethylene). The polymers can be cross-linked
by application of radiation such as e-beam, UV, gamma, x-ray radiation or by heat-
activated chemical crosslinking techniques. Radiation techniques provide the advantage
that the polymer typically does not have to be substantially heated to achieve
crosslinking. For e-beam radiation, an exposure of about 200-300, e.g. 250 kilograys,
typically provides sufficient crosslinking.

Brief Description of the Drawings

FIGURE 1 illustrates graphically the DMA plots of the TMP POSS based thermoplastic polyurethane (TPU) with mole ratio of PEG : POSS as 1:6, 1:4 respectively;

FIGURE 2 illustrates graphically the DSC results of TMP POSS based TPU with different PEG : POSS mole ratios;

FIGURE 3 illustrates the equipment as used for measuring stress-strain; and

FIGURE 4 illustrates graphically the stress-strain plot of the TMP POSS based TPU (PEG : POSS = 1.6).

Detailed Description

Thermoplastic polyurethanes with different compositions were synthesized by one-step condensation polymerization using the scheme shown above. Toluene was used as solvent and dibutyltin dilaurate was used as catalyst. The reaction was kept at 90 °C under the nitrogen for 2 hours and then cooled down to room temperature and precipitated into hexane. The product was dried thoroughly and dissolved in toluene to make a 10wt% solution for casting films. The molecular weights and molecular weight distributions of this series of samples obtained from size exclusion chromatography are summarized in Table 1.

Table 1. Molecular weights and molecular weight distributions of POSS-
based polyurethanes having polyol (PEG) block length of 10000 g/mol

Sample	M_n (g/mol)	M_w/M_n
PEG:POSS = 1:3	47,400	1.42
PEG:POSS = 1:4	48,800	1.44
PEG:POSS = 1:6	54,000	1.54
PEG:POSS = 1:8	49,200	1.30

Samples of polyurethanes with different compositions were characterized by differential scanning calorimetry (TA Instruments DSC2920). All of the samples were characterized under the same conditions: two scans were performed for each sample with heating and cooling rates of 10 °C/min (Figure 2). It was observed that this series of polyurethanes exhibit two melting points, one in the range $45 < T_{m1} < 50$ °C corresponding to the melting temperature of PEG "soft" block. The other melting transition appears in the range $110 < T_{m2} < 130$ °C, which corresponds to the melting of a POSS-reinforced hard segment phase. The melting temperature of the soft segment is observed to shift to lower values with a broadening of the melting peak while the melting temperature of the hard segment is observed to shift to higher values with a sharpening of the melting peak when the mole ratio of polyol:chain extender decreases. This result can be explained in that as the PEG : POSS ratio decreases, the resulting block copolymer will have less overall PEG content, which will directly affect the size and perfection of the crystallization of PEG blocks. Therefore, the melting temperature moves to lower values and the peak is broadened. On the contrary, the content of POSS will increase in the block copolymers, which provides for more clear aggregation of hard segments to form larger and more perfect crystals. Therefore, the melting temperature of hard segment moves to higher values while the peak is sharpened (Figure 2).

The dried films of the formed polyurethanes were cut into thin strips for tests of temporary shape fixing and subsequent recovery, or shape memory. For example, a sample was first heated on the hot stage to 65 °C, which is well above the first transition temperature but low enough to avoid melting of the elastic network of the POSS-rich phase. It was then stretched to a certain degree of elongation and cooled down to the room temperature. The deformed shape was fixed at room temperature. Finally, the deformed sample was heated up again on hot plate to 65 °C and it was observed that the sample restored to its original length completely and within seconds. A similar phenomenon was observed when water was used as a stimulus for the shape recovery except that the sample secondarily swelled to form a tough hydrogel.

The hybrid polyurethanes of the disclosure can be used for the following applications.

    a.   Stents, patches and other implants for human health care

    b.   Surgical tools requiring adjustable shape but high stiffness.

    c.   Arbitrarily shape-adjustable structural implements, including personal care items (dinnerware, brushes, etc.) and hardware tool handles.

    d.   Self healing plastics

    e.   Medical devices (a dented panel is repaired by heating or plasticizing with solvent)

    f.   Drug delivery matrices

    g.   High-strength thermoplastic (non-crosslinked) superabsorbant hydrogels

    h.   Aqueous rheological modifiers for paints, detergents and personal care products

    i.   Impression material for molding, duplication, rapid prototyping, dentistry, and figure-printing.

    j.   Toys

    k.   Reversible Embossing for information storage

    l.   Temperature and moisture sensors

    m.   Safety valve

    n.   Heat shrink tapes or seals

    o.   Heat controlled Couplings and fasteners

    p.   Large strain, large force actuators

    q.   Coatings, adhesives

    r.   Textiles, clothing

The shape memory polymers of the disclosure are particularly suitable as biomaterials because of their low thromogenicity, high biocompatibility, as well as unique mechanical properties. In accordance with the disclosure the shape memory polyurethanes were formulated such that the melting temperature of one segment falls within a useful temperature range for biomedical application: 37 °C-50 °C.

The present disclosure provides an advantageous shape memory polymer that includes thermoplastic polyurethane shape memory polymers formed by reacting in one step a polyol, a POSS chain extender and a diisocyanate, having medium and tunable modulus in the fixed state at room temperature having a tunable sharp transition, whose permanent shape can be repeatedly remolded above a certain melting temperature.

Although the polymers and processing methodologies of the present disclosure have been described with reference to specific exemplary embodiments thereof, the present disclosure is not to be limited to such exemplary embodiments. Rather, as will be readily apparent to persons skilled in the art, the teachings of the present disclosure are susceptible to many implementations and/or applications, without departing from either the spirit or the scope of the present disclosure. Indeed, modifications and/or changes in the selection of specific polymers, polymer ratios, processing conditions, and end-use applications are contemplated hereby, and such modifications and/.or changes are encompassed within the scope of the present invention as set forth bh the claims which follow.
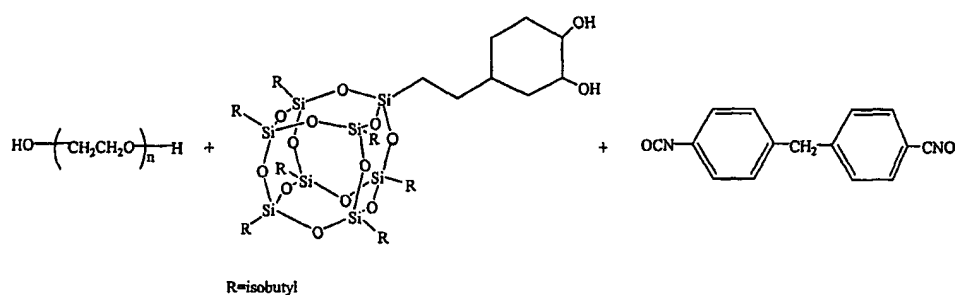
CLAIMS:

1.   A method for making a thermoplastic polyurethane shape memory polymer comprising reacting in one step (A) a polyol, (B) a POSS chain extender and (C) a diisocyanate.

2.   The method of claim 1 wherein the polyol is a member selected from the group consisting of polyethylene glycol (PEG), polycaprolactone (PCL), polycyclooctene (PCO), trans-1,4 butadiene, transisoprene, polynorbornene diol and polymethacrylate copolymer.

3.   The method of claim 1 wherein the polyol is a member selected from the group consisting of polyethylene glycol, polycaprolactone, polycyclooctene, trans-1,4-butadiene and transisoprene and is semicrystalline.

4.   The method of claim 1 wherein the polyol is an amorphous diol having a Tg in the range of 20 - 80 °C, and is a member selected from the group consisting of polynorbornene diol and polymethacrylate copolymer diol.

5.   The method of claim 1 wherein the POSS chain extender is a member selected from the group consisting of TMP cyclopentyldiol-POSS, TMP cyclohexyldiol-POSS, TMP isobutyldiol-POSS, trans-cyclohexanediolcyclohexane-POSS and transcyclohexanediolisobutyl-POSS.

6.   The method of claim 1 wherein the diisocyanate is a member selected from the group consisting of 4,4'-diphenyl methylene diisocyanate, toluene-2,4-diisocyanate (TDI), toluene-2,6diisocyanate, hexamethylene-1,6-diisocyanate (HDI), 4,4'diphenylmethane diisocyanate (MDI), isophorone diisocyanate (IPDI), and hydrogenate 4,4'-diphenylmethane diisocyanate (H12MDI).

7.   The method of claim 1 wherein the diisocyanate is 4,4'-diphenyl methylene diisocyanate.

8.   The method of claim 1 wherein the polyol is a member selected from the group consisting of polyethylene glycol, polycaprolactone, polycyclooctene, trans-1,4-butadiene

and transisoprene, the POSS chain extender is a member selected from the group
consisting of TMP cyclopentyldiol-POSS, TMP cyclohexyldiol-POSS, TMP
isobutyldiol-POSS, trans-cyclohexanediolcyclohexane-POSS and
transcyclohexanediolisobutyl-POSS and the diisocyanate is 4,4'-diphenyl methylene
diisocyanate.

9.   The method of claim 8 wherein said reaction is carried out in presence of
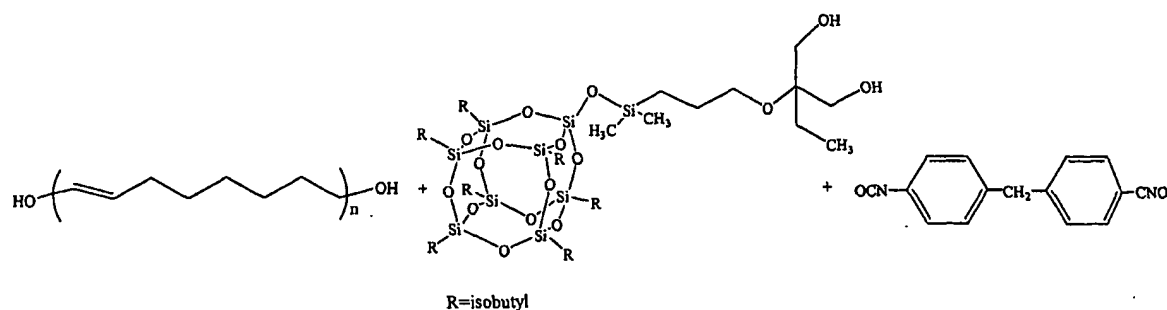dibutyltin dilaurate as catalyst.

10.   The method of claim 1 wherein the reaction is carried out according to the
following reaction scheme

11.   The method of claim 1 wherein the reaction is carried out according to the
following reaction scheme
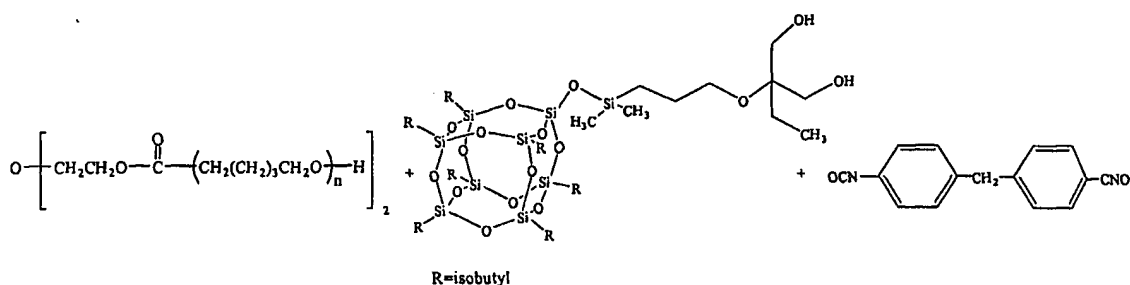
12.   The method of claim 1 wherein the reaction is carried out to the following reaction scheme

R=isobutyl

13.   A thermoplastic polyurethane shape memory polymer prepared by the method of claim 1.

14.   A thermoplastic polyurethane shape memory polymer prepared by the method of claim 8.

15.   A thermoplastic polyurethane shape memory polymer prepared by the method of claim 9.

16.   A thermoplastic polyurethane shape memory polymer prepared by the method of claim 10.

17.   A thermoplastic polyurethane shape memory polymer prepared by the method of claim 11.

18.   A thermoplastic polyurethane shape memory polymer according to claim 1 containing a filler which is a member selected from the group consisting of boron nitride, silica, titanium dioxide, montmullinite, clay, Kevlar, staple, aluminum nitride, barium and bismuth subcarbonate.

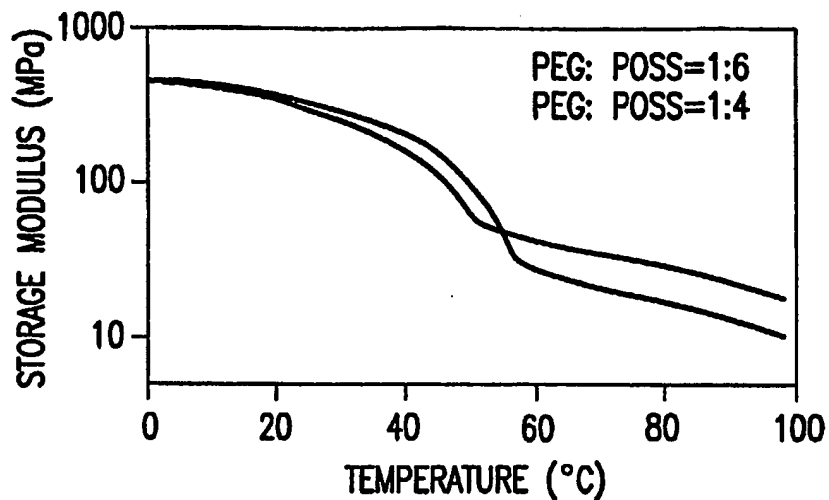19.   A thermoplastic polyurethane shape memory polymer having the formula
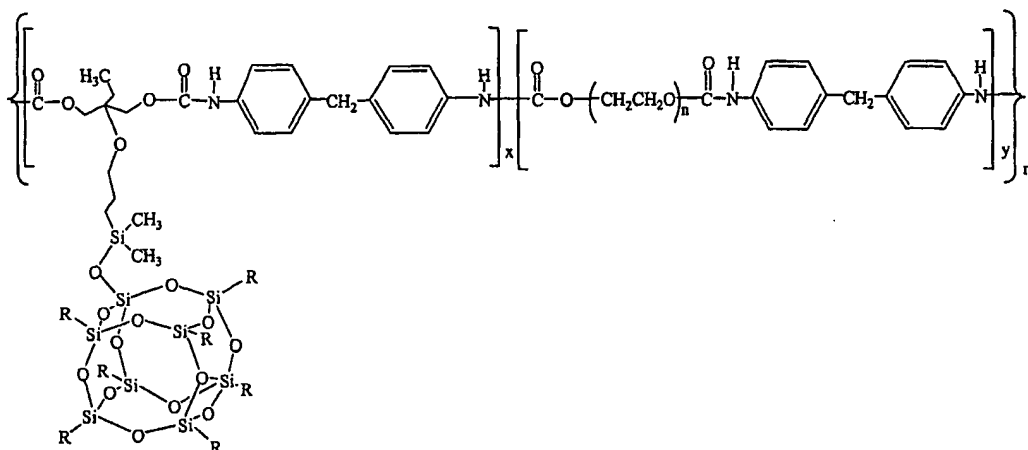
wherein the ratio of X : Y is 1 to 20, the polyol degree of polymerization is 1 < n <1000

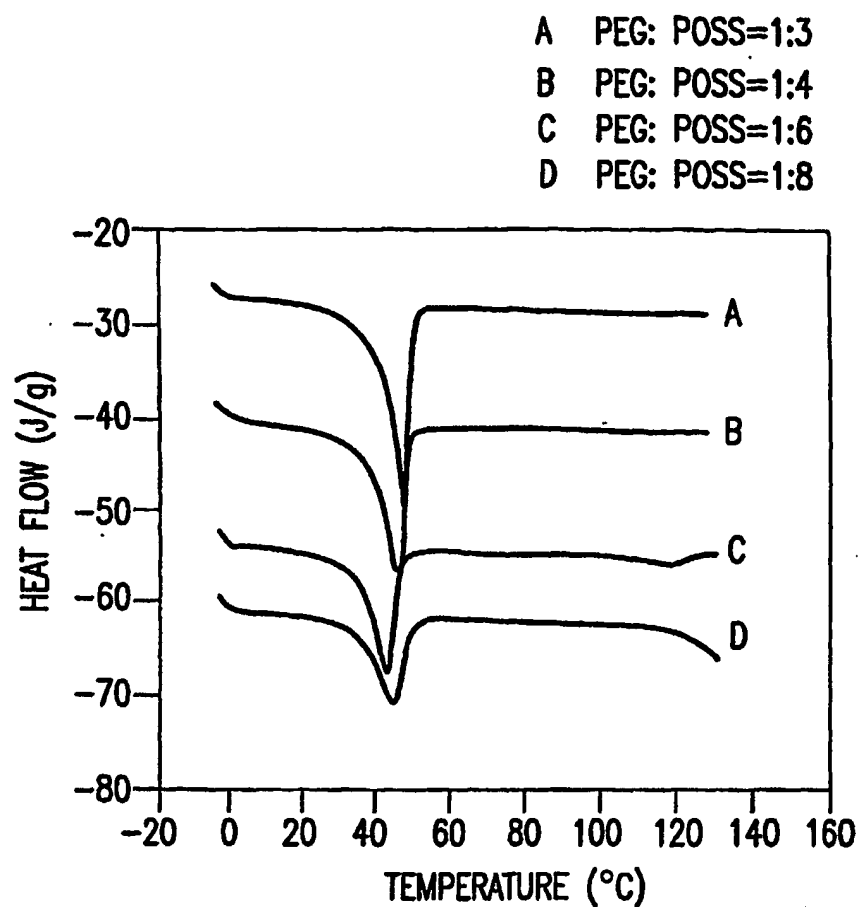and the total degree of polymerization, 2 <m< 100.

1/3

DMA plots of the TMP POSS based TPU, with mole ratio of
PEG : POSS as 1:6, 1:4 respectively. A transition temperature
around 45–47°C was observed. A typical plateau corresponding
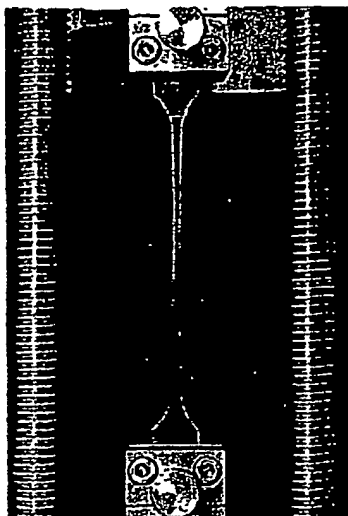to physically crosslinked polymers was observed also.

FIG.1

A   PEG: POSS=1:3
B   PEG: POSS=1:4
C   PEG: POSS=1:6
D   PEG: POSS=1:8

DSC results of TMP POSS based TPU with different PEG: POSS mole ratio. Two melting peaks can be observed indicating the microphase separation between the soft and hard segment.

FIG.2

Stress–strain experiment of the TMP POSS based
TPU (PEG: POSS=1:6) according to ASTM standard.
A dumbell shaped sample having the
length of the narrow part as 9.42 mm, distance
between grips as 25.5 mm and thickness as
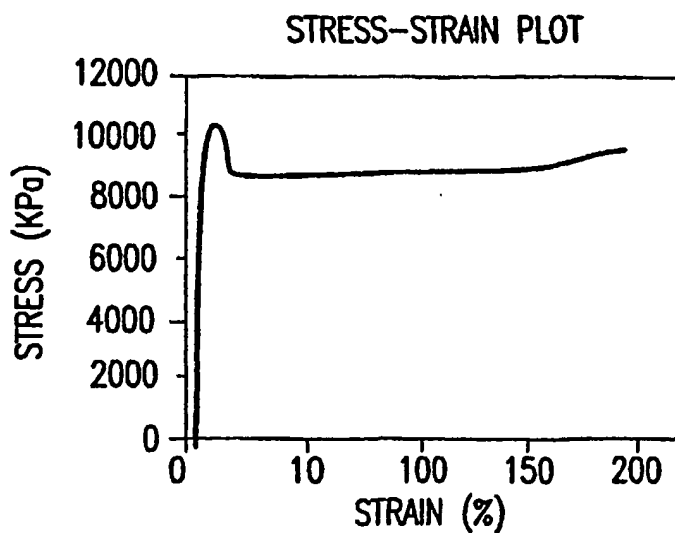0.355 mm was stretched at room temperature, 1 mm/min.

FIG.3

STRESS–STRAIN PLOT

FIG.4